

(12) **UK Patent Application** (19) **GB** (11)

2 137 627 A

(43) Application published 10 Oct 1984

(21) Application No **8408335**

(22) Date of filing **30 Mar 1984**

(30) Priority data

(31) **8308722**

(32) **30 Mar 1983**

(33) **GB**

(51) INT CL³
C08G 59/14

(52) Domestic classification
C3B 1D2C 1N10 1N1A C
U1S 1367 1384 3011 3042 3043 3045 C3B

(56) Documents cited
GB 1546256 GB 1483235 GB 1480487
GB 1407851 GB 1178732 EP 0041108

(58) Field of search
C3B

(71) Applicants
Evode Limited (United Kingdom)
Common Road, Stafford, ST16 3EH

(72) Inventor
Robert Sydney Whitehouse

(74) Agent and/or Address for Service
P. David Lishman, Aston Farm House, Newtown Lane,
Shustoke, Coleshill, Warwickshire B46 2SD

(54) **Epoxide resin compositions**

(57) Curable epoxide resin compositions having improved mechanical and fire-resistant properties comprise an epoxide resin adducted with an elastomeric polymer including a chlorinated monomer such as a chlorinated butadiene, vinyl chloride or vinylidene chloride and an unsaturated carboxylic acid monomer such as acrylic acid or methacrylic acid. The composition may be produced by stirring an aqueous latex of the polymer into the liquid resin, with heating if necessary. The compositions can be cured with conventional curing agents and can replace ordinary epoxide resins in most applications without any change in procedure.

GB 2 137 627 A

SPECIFICATION

Epoxide resin compositions

- 5 Epoxide resins are widely used as structural adhesives. They produce strong bonds with a wide variety of substrates. However, they are hard material with low elongation and poor resistance to impact and flexural forces. These mechanical properties, and their high flammability, make them unsuitable for use for certain purposes for which they are otherwise well-suited.

- Various attempts have been made to produce epoxide resin compositions with improved mechanical properties. Examples are described in U.S. Patents Nos. 3,297,622, 3,316,195, 3,806,483 and 4,128,519. A paper by Trostyanskaya, Babayevskii and Kulik in "Polymer Science U.S.S.R." Vol. 21 pp 1456-1462 describes how epoxidised rubber latices can be incorporated into an epoxide resin using the compatibility provided by the epoxide functional groups and then co-reacting with these functional groups to produce a bonded matrix. Other attempts to improve the mechanical properties of epoxide resins have involved the incorporation of liquid nitrile rubber or the use of particular curing agents. However, the resulting compositions usually have inferior ultimate strength and a lower heat distortion temperature than unmodified resins.
- The flammability of epoxide resins has been reduced by incorporating a halogen into the backbone of the resin structure, for example by the use of brominated bisphenol-A in the reaction mixture for producing the resins. Alternatively, conventional fire-retardants such as halogenated compounds, aluminium trihydrate, antimony compounds or phosphorus compounds may be incorporated in the resins. These additives, however, may have undesirable effects on the other properties, for example lowering the heat distortion temperature.

- According to this invention, a curable epoxide resin composition comprises an epoxide resin adducted with an elastomeric polymer including at least one chlorinated monomer and at least one unsaturated carboxylic acid monomer.

- The epoxide resin composition may include more than one epoxide resin and/or more than one elastomeric polymer.

- Chlorinated monomers suitable for use in performing the invention are chlorinated butadienes, vinyl chloride and vinylidene chloride. Preferred unsaturated carboxylic acids are acrylic acid and methacrylic acid. The carboxylic acid concentration in the polymer should be between 0.5 and 10 per cent and typically is between 1 and 5 per cent.

- Suitable elastomeric polymers may include more than one chlorinated monomer and/or more than one unsaturated carboxylic acid monomer.

- Suitable epoxide resins include bisphenol-A and bisphenol-F types, epoxy-novalak resins and brominated and alicyclic epoxides. The compositions may include more than one such resin.

- The invention includes a method of manufacture of such an epoxide resin composition comprising the steps of stirring an aqueous latex of the elastomeric

polymer or polymers into the epoxide resin or blend of epoxide resins in liquid state and removing the water.

- On removal of the water, adducting reaction takes place between the carboxylic acid groups on the polymer or polymers and epoxide linkages on the epoxide resin or resins, producing the curable epoxide resin composition. The resin or resins must be present in sufficient quantity to ensure that the whole of the polymer or polymers is/are adducted, and is/are preferably present in excess. The product of the adducting reaction is soluble in the resin or resins, so in this case a stable homogeneous solution of the composition in the uncombined excess resin is produced.

- If the epoxide resin or blend of resins is sufficiently mobile at temperature below 100°C, the first step, of stirring the polymer latex into the liquid resin or resin blend at room temperature, will produce a substantially uniform dispersion of polymer latex particles in the liquid resin matrix. Then, in the second step, the mixture is heated above 100°C to drive off the water. This method may be modified for less mobile resins by first heating the resin or resin blend to a sufficiently mobile state in a pressure vessel and increasing the pressure to raise the boiling point of water above the temperature of the resin before adding the polymer latex and stirring to produce a dispersion as before. After mixing, the temperature may be raised above the boiling point or the pressure be reduced to lower the boiling point below the temperature of the mixture in order to remove the water by boiling.

- In carrying out this method, mixing may be facilitated by pre-heating the polymer latex to a temperature below the relevant boiling point of water before adding it to the resin.

- This method may not be satisfactory where high proportions, approaching 50 per cent, of the elastomeric polymer or polymers is/are required in the finished composition. Coagulation of the polymer or polymer blend may occur as the water is being removed, and this will prevent completion of the adducting reaction.

- In an alternative method, both steps of the invention are performed simultaneously. The resin or resin blend is heated to a temperature above 100°C and is agitated rapidly whilst the polymer latex is slowly added. The water is immediately volatilised and flashed off and the polymer or polymers is/are intimately mixed with the liquid resin whereupon the adducting reaction takes place. Again, the polymer latex may be pre-heated, and the pressure may be regulated to enable the method to be performed at a lower or higher temperature if this is necessary to provide adequate mobility in the resin or resin blend or to avoid coagulation or thermal decomposition of the polymer or polymer blend before the adducting reaction is completed.

- The curable epoxide resin composition produced by the adducting reaction may be cured, like the original epoxide resin or resins, by use of conventional curing agents such as amines, polyamides, anhydrides or boron trifluoride adducts. On curing, the polymer separates out of the composition, forming discrete spheres in a matrix of cured resin. These improve the mechanical properties of the cured mass, in particular

resisting crack development.

By particular selection of the elastic polymer or polymers used, the viscosity of the curable composition produced may be increased substantially compared with the original resin. Delayed action curing agents may be incorporated in the resin in the production of such viscous compositions, which are then useful as heat curable hot melt systems.

The presence of a chlorinated monomer in a polymer increases its compatibility with epoxy resins. In the method of the invention the presence of a chlorinated monomer assists in the establishment of a uniform dispersion of the polymer latex particles in the resin and promotes the adducting reaction. The chlorinated monomer furthermore reduces the flammability of the curable epoxide resin compositions produced by the reaction and reduces their water absorption as compared with the original epoxide resins used. Reduction of water absorption improves the strength of the cured compositions under conditions of high humidity.

Four examples of curable epoxide resin compositions were produced using a conventional bisphenol-A type epoxide resin produced by Dow Chemical Company under their reference DER 330 and four different polymer latices. This resin is liquid at normal room temperatures and the compositions were produced by the first method described above, that is by stirring each polymer latex into a quantity of the resin to produce a uniform dispersion and then heating to remove the water and allowing the resultant composition to cool. The polymer latices added, expressed as parts by weight of dry polymer per hundred parts of resin (phr) were as follows:—

1. Haloflex 202 (Imperial Chemical Industries P.L.C.)—an emulsion of a terpolymer including vinylidene chloride, vinyl chloride, an alkyl acrylate or alkyl methacrylate and an unsaturated carboxylic acid monomers—20 parts.
2. Polidene 33075 (Scott Bader P.L.C.)—an emulsion of a polymer including vinylidene chloride and acrylate monomers—20 parts.
3. Baypren 4R (Bayer AG)—anionic carboxylated polychloroprene and methacrylic acid latex—10 parts.
4. Neoprene Latex 115 (Du Pont)—non-ionic carboxylated polychloroprene and methacrylic acid latex—30 parts.

Standard 25mm × 25mm overlap test joints were made with the resin DER 330 and each of the compositions produced as above, in each case blending in 5 phr of Ancaflex 1171 (Anchor Chemical Company) a boron trifluoride adduct curing agent, and the joints were conventionally cured for 2 hours at 50°C followed by 2 hours at 100°C. Shear strength tests on the cured joints produced the following results:—

The cured joints were loaded in shear and the loads (Newtons) at failure were:—

Resin DER 330	3550
Composition 1	6550
Composition 2	9730
Composition 3	7730
Composition 4	6940

Haloflex, Polidene, Baypren, Neoprene and Ancaflex are Registered Trade Marks.

Curable epoxide resin compositions according to the invention may be used in place of ordinary epoxide resins in most of their usual industrial applications, generally without any change in procedure, with beneficial results. In mechanical structures including elements such as joints or structural components produced by curing a curable epoxide resin composition according to the invention, improvements are likely to be found in specific adhesion, tensile strength, impact resistance and resistance to crack development as well as in reduced flammability of the elements.

CLAIMS

1. A curable epoxide resin composition comprising at least one epoxide resin adducted with at least one elastomeric polymer, the or each elastomeric polymer including a chlorinated monomer and an unsaturated carboxylic acid monomer.
2. A curable epoxide resin composition as claimed in Claim 1 wherein the or an elastomeric polymer includes more than one chlorinated monomer and/or more than one unsaturated carboxylic acid monomer.
3. A curable epoxide resin composition as claimed in claim 1 or Claim 2 wherein the chlorinated monomer or monomers is/are selected from a chlorinated butadiene, vinyl chloride and vinylidene chloride.
4. A curable epoxide resin composition as claimed in any of Claims 1 to 3 wherein the or each unsaturated carboxylic acid monomer is acrylic acid or methacrylic acid.
5. A curable epoxide resin composition as claimed in any preceding claim which is in homogeneous solution with uncombined epoxide resin or resins.
6. Method of manufacture of a curable epoxide resin composition as claimed in any preceding claim comprising the steps of stirring an aqueous latex of the elastomeric polymer or polymers into the epoxide resin or resins in liquid state and removing the water.
7. Method as claimed in Claim 6 including the preliminary step of heating the epoxide resin or resins to render it or them liquid.
8. Method as claimed in Claim 6 or Claim 7 wherein the water is removed by heating after stirring in the aqueous latex.
9. Method as claimed in Claim 6 including the preliminary step of heating the epoxide resin or resins to a temperature above the boiling point of water at the ambient pressure whereby the water is removed by evaporation simultaneously with the step of stirring in the aqueous latex.
10. A mechanical structure including an element produced by curing a curable epoxide resin composition as claimed in any of Claims 1 to 5.

Printed in the United Kingdom for Her Majesty's Stationery Office, 8818935, 10/84, 18996. Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY, from which copies may be obtained.

BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)